

**JAROSITE IN THE SHERGOTTITE QUE 94201.** D.K. Ross<sup>1</sup>, M. Ito<sup>2,4</sup>, M.N. Rao<sup>1</sup>, R. Hervig<sup>3</sup>, L.B. Williams<sup>3</sup>, L. E. Nyquist<sup>4</sup> and A. Peslier<sup>1</sup> 1. Jacobs Technology, Houston Tx. 77258-8447. 2. Lunar and Planetary Institute-USRA, 3600 Bay Area Blvd. Houston Tx 77058 3. SESE-Arizona State University, Tempe AZ. 85287 4. NASA Johnson Space Center, NASA Parkway 77058. Daniel.Ross@nasa.gov

**Introduction:** Veins of the hydroxylated, potassium ferric sulfate mineral jarosite -  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  - have been identified in the martian meteorite Queen Alexandra Range (QUE) 94201. Iron potassium sulfate had been reported in QUE 94201 by Wentworth and Gooding [1]. Jarosite has been reported in other Martian meteorites - Roberts Massif (RBT) 04262 [2], Miller Range (MIL) 03346 [3,4], and Yamato 000593 [5] - and it has been identified on the Martian surface by Mössbauer spectroscopy [6]. Given the presence of jarosite on Mars, and the burgeoning interest in water-rock interactions on Mars, the question arises whether jarosite in Martian meteorites is formed by aqueous alteration on Mars, or in Antarctica.

Hydrogen isotopes are potentially sensitive indicators of the site of formation or last equilibration of hydrous alteration minerals, because of the large difference between D/H ratio of the Martian atmosphere (and also presumably the cryosphere) and terrestrial hydrogen. The Martian atmospheric  $\delta\text{D}_{\text{SMOW}}$  ratio is  $\sim +4200\text{‰}$  [7], igneous minerals with substantial hydrogen (phosphates) have high  $\delta\text{D}$ ,  $\sim +2000\text{‰}$  to  $+4700\text{‰}$  [8 and references therein] versus terrestrial waters with  $\sim -480\text{‰}$  to  $+130\text{‰}$  [9]. The crystal chemistry and structure of jarosite are reviewed in Papike et al. [10].

Here we report hydrogen isotopes measured in jarosite in QUE 94201 by ion microprobe, and also report on the major element composition of jarosite measured by electron microprobe.

**Mineral Chemistry of Jarosite:** We analyzed the largest vein of jarosite observed in thin section QUE 94201,38, which is shown in x-ray maps in Fig. 1 and backscattered electron image in Fig. 2. The CAMECA SX100 electron probe at NASA-JSC was used to acquire the x-ray maps and to collect quantitative data on jarosite compositions. Jarosite investigated in this study has substitution of Na for K,  $\text{Al}^{3+}$  for  $\text{Fe}^{3+}$  and phosphate for sulfate. This phase is difficult to analyze by electron probe because of beam-induced damage and mobilization of alkalis. The beam accelerating voltage was 15 kV, with a 20 nA beam current. Hindsight suggests that a 10 nA beam current would permit analysis with diminished beam damage and/or a more focused electron beam. We noted that data collected with a 5 micron defocused beam had significantly less alkalis - both Na and K - compared to data collected with a 10 micron defocused beam, due to beam-induced alkali

mobilization. An additional complication is that the alkali site in the structure can be occupied by the hydronium ion -  $\text{H}_3\text{O}^+$ , so that the alkalis will not necessarily sum to a stoichiometric amount. We also noted the presence of a minor P peak in EDS data collected on this jarosite (phosphate groups substituting for sulfate), although P had not been included in the quantitative, WDS data collection. Further electron probe work will be needed to refine analytical parameters and yield final, definitive results on the composition of jarosite in this meteorite. Our best averaged result for its composition (derived from data collected with a 10 micron defocused electron beam) is  $(\text{K}_{0.39}\text{Na}_{0.40}\text{H}_3\text{O}^{+0.21})(\text{Fe}_{2.82}\text{Al}_{0.11})(\text{SO}_4)_2(\text{OH})_6$ . The hydronium ion concentration is calculated by difference and must be viewed as an upper limit. H content in the hydroxyl site was calculated from the ideal formula (1.21 wt. % H), fixed in matrix correction calculations, and the oxygen needed to charge balance was calculated based on stoichiometry. The structural formula shown was calculated by setting S at 2.0 atoms per formula.

**Hydrogen Isotopes:** Hydrogen isotopic analyses of jarosite in QUE 94201 were performed, *in situ*, using the IMS-6f ion microprobe at Arizona State University. A  $\text{Cs}^+$  primary ion beam with a diameter of  $\sim 3\text{-}5\text{ }\mu\text{m}$  was used. The primary beam current was  $\sim 0.4\text{ nA}$ . Negative secondary ions of  $^1\text{H}$  and D were measured by a single electron multiplier (EM) detector in peak-switching mode at a mass resolution of  $M/\Delta M = \sim 600$ . Count rates of H ions were  $1.4$  to  $6.8 \times 10^5$  in jarosite. Count rates were limited in order to minimize deadtime effects on the EM. The deadtime was 42 ns, and deadtime corrections were applied to the data. An incident electron-flooding gun and carbon coat on the sample surface prevented sample charging. Instrumental mass fractionation correction was made using terrestrial standards of macusanite glasses [11] and San Carlos kaersutitic amphibole [12] with different  $\text{H}_2\text{O}$  wt % and known DH ratios

The results of our hydrogen isotope measurements are  $\delta\text{D}_{\text{SMOW}} -386 \pm 29\text{‰}$ ,  $-343 \pm 32\text{‰}$ , and  $-325 \pm 39\text{‰}$  ( $2\sigma$  mean). Greenwood and coworkers [2] reported  $\delta\text{D}_{\text{SMOW}}$  of  $-488\text{‰}$  and  $-476\text{‰}$  in jarosite in RBT 04262. Our results are broadly consistent with those previously reported but are somewhat less depleted in deuterium. Greenwood et al. supported the formation of jarosite in

Antarctica, but also noted the possibility that jarosite could have formed on Mars and then re-equilibrated with respect to H isotopes in terrestrial waters. Our results also indicate that jarosite formed in Antarctica, or that Martian jarosite almost completely re-equilibrated with terrestrial hydrogen.

**References:** [1] Wentworth S.J. and Gooding J.L. (1996) *LPSC XXVII*, p. 1421. [2] Greenwood J.P. et al. (2009) *LPSC XL*, abs. #2528. [3] Vicenzi E.P. et al. (2007) *LPSC XXXVIII*, abs. # 2335. [4] McCubbin F.M. et al. (2009) *Geochim. Cosmochim. Acta*, 73, 4907-17. [5] Noguchi T. et al. (2009) *J. Geophys. Res.* 114, E10004. [6] Klingelhöfer G. et al. (2004) *Science*, 1740-45. [7] Bjoraker et al. (1989) *Bull. Amer. Astron. Soc.* 21, 991. [8] Greenwood J.P. et al. (2008) *Geophys. Res. Lett.*, 35, L05203. [9] Papike J.J. et al. (2006) *Geochim. Cosmochim. Acta*, 70, 1309-21. [10] Hoefs, J. (2004) *Stable Isotope Geochemistry*. [11] Pichavant M. et al. (1987) *Geochem. Soc. Spec. Pub.* 1, 359-73 ; [12] Poreda, R.J. and Basu, A.R. (1984) *EPSL* 69, 58-68.

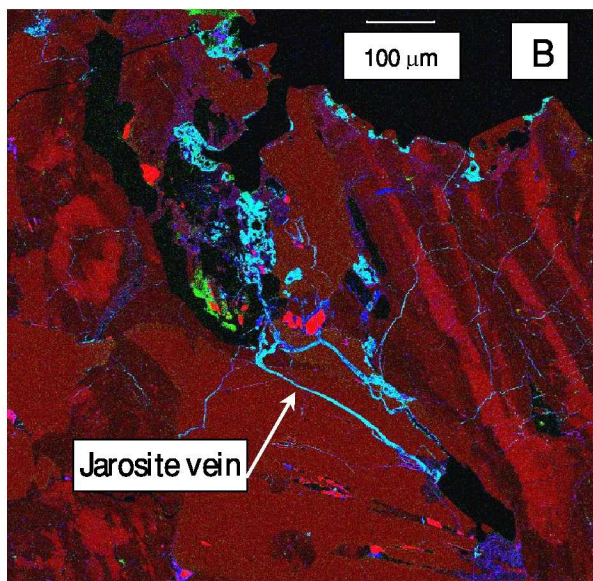
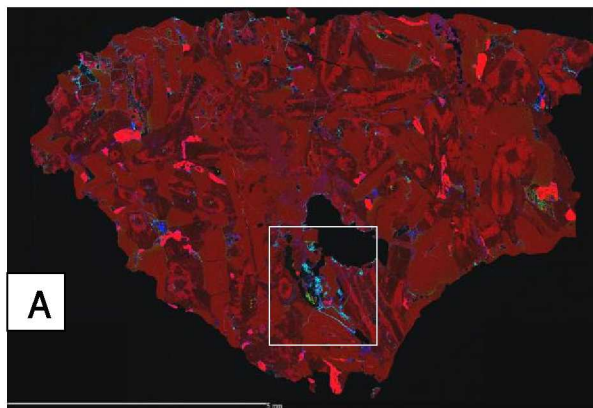


Figure 1. X-ray maps of QUE 94201,38: overlays with Ca - red, K - green and S - blue. Jarosite contains both S and K and thus appears pale blue in these maps. Black areas are epoxy (large area above jarosite) or other phases, such as Fe-Ti oxides that have no Ca, K or S. A. Map of whole thin section. B. Close-up of jarosite vein analyzed in this study. The jarosite vein studied here is ~ 5-20 microns in width.

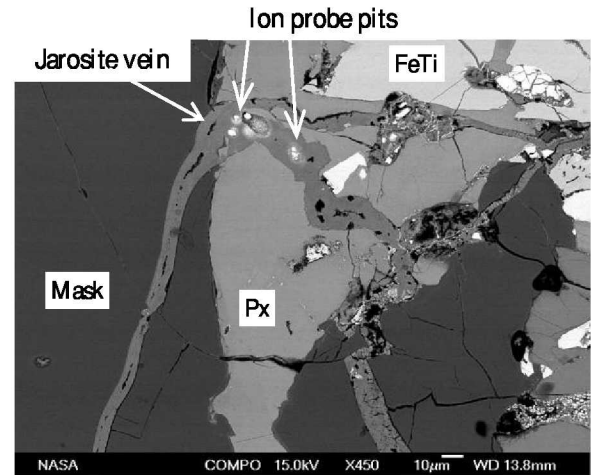


Figure 2. Backscattered electron image of part of the jarosite vein showing the location of 2 ion probed locations. Labels: Mask is maskelynite, Px is pyroxene, FeTi is iron-titanium oxide.